

CONSIDERATION ON BOND CLEAVAGE REACTIONS OF BRIDGE STRUCTURE IN COAL MODELS AND COAL WITH TWO DIFFERENT HYDROGEN DONATING COMPOUNDS

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Key words: bond cleavage, coal models, hydrogen donating compounds

INTRODUCTION

Coal organic material (COM) is believed to be an amorphous polymer consisting aromatic clusters with aliphatic side chains or bridges including naphthenic portion. Accordingly, COM should be described by certain chemical formula as other polymers are. Using various analytical methods coal chemical structure had been investigated in detail, however, COM is essentially far from the ordinal polymer. It does not contain any repeated units but many moieties and shows different behavior in its conversion reaction depending on its rank or its mining region. From these complexities, information concerning its chemical structure and reactivity is now still limited.

In coal utilization processes such as liquefaction, gasification or carbonization, decomposition of COM should be important. Judging from the accepted chemical structures for COM, the bond cleavage reaction of the bridge structure plays an important role in its decomposition. Now, we focus on this bond cleavage reaction in coal because this is one of the important reactions during heat-treatment of coal. There are many investigations which consider the coal models having the bridge structures as contained in coal and pursue the fashion of the reaction using the model compounds. Autrey et al.[1], Futamura et al.[2] and Nomura et al.[3] had mentioned the pyrolysis or hydrogenolysis of diarylmethane, while Korobkov et al.[4] reported the rate constants of thermolysis of diaryl or alkylethers in detail and discussed about their mechanisms. As to the behavior of side chains, Savage et al.[5] examined 1-alkylpyrene pyrolysis, and Nomura et al.[6] and Freund et al.[7] picked up the aromatic compounds having longer bridges or alkyl side chains. As to the mechanisms of the bond cleavage reactions occurred in coal, McMillen et al. proposed radical hydrogen transfer (RHT), which was also discussed by other researchers[1,8,9].

In a previous paper[10], we investigated the chemical structure change of coal during its carbonization process and pointed out the importance of the amount of the transferable hydrogen for development of coal plasticity. This seems to be parallel with many researcher's intentions. Here, by using DHA and DHP as the hydroaromatics, we considered two types of the bond cleavage reactions, the homolytic cleavage and the ipso position cleavage.

EXPERIMENTAL SECTION

Samples.

Coal samples employed in this work are the six kinds of bituminous coals, provided by the Iron and Steel Institute of Japan. The characteristics are summarized in Table 1. These coal samples were pulverized (-100 mesh) and dried at 100 °C for 6 h in vacuo prior to use. The substrates of model compounds 1,2-di(1-naphthyl)ethane (DNE) and 1,5-dibenzyl-naphthalene (DBN), were synthesized as follows: DNE was prepared by reduction of (1-chloromethyl)naphthalene with iron powder in water and DBN was obtained by $\text{Et}_3\text{SiH}/\text{CF}_3\text{COOH}$ reduction of 1,5-dibenzoylnaphthalene according to the method reported[3]. The other reagents or coal model compounds were commercially available and purified by recrystallization before use.

The heat-treatment of coal or its model compounds in the presence of hydrogen donating compounds.

A coal sample and 9,10-dihydroanthracene (abbreviated as DHA) or 9,10-dihydrophenanthrene (DHP) were put in a sealed tube (Pyrex, 6 mm inner diameter x 100 mm long) at the weight ratio of 1:1 (100 mg each), the tube being inserted into the electric furnace preheated at determined temperature (380 or 420 °C), and kept for 5 min. The temperature of the inside of the sealed tube was found to raise to the desired temperature within 2 min, the heating rate being about 200 K/min. After 5 min passed, the sealed tube was taken out and the products were recovered by breaking the tube and washing the inside of the tube with dichloromethane. After the addition of an appropriate internal standard, the amounts of DHA or DHP consumed were determined.

In the case of the model compounds [1,2-diphenylethane (DPE), benzylphenylether (BPE), 1,2-di(1-naphthyl)ethane (DNE) and 1,5-dibenzyl-naphthalene (DBN)], 0.25 mmol of the hydrogen donating compounds and each model compound were heated under the similar conditions to those mentioned above. Qualitative and quantitative analyses of the products were undertaken by a Shimadzu QP-2000A GC/MS and a Shimadzu GC-14APSFSC gas chromatograph with CBP-1 column (0.25 mm diameter x 25 m long), respectively. Duplicate runs, at least three times, were made for each set of the reaction to insure reproducibility.

RESULTS AND DISCUSSION

The reaction of coal with hydrogen donating compound.

The heat-treatment of the six sample coals with the hydrogen donating compounds, DHA or DHP was carried out at 380 or 420 °C for 5 min. The reaction gave the corresponding dehydrogenated compound, anthracene or phenanthrene, as the major product along with minor amounts of tetrahydro-derivatives (mainly 1,2,3,4-tetrahydro isomer). When either DHA or DHP was treated in a sealed tube without coal (blank runs), there observed negligible amounts of tetrahydro-derivatives. These results suggest tetrahydro-derivatives to be derived from coal-catalyzed disproportionation of DHA or DHP.

We evaluated the amounts of hydrogen transferred from DHA or DHP to coal according to the following equation:

$$\frac{\text{The amount of hydrogen transferred (mg H}_2\text{/g daf coal)}}{(\text{mg}) \times 2/178 - \text{wt. of tetrahydro-derivatives (mg)} \times 2/182} \times 1000/\text{wt. of daf coal (mg)}$$

The results of the reaction of coal with the hydrogen donating compounds are shown in Figure 1. The lower the rank of the coals was, the more amounts of hydrogen were consumed. As we had already reported, the chemistry in the reaction at around 400 °C was considered as the bond cleavage reactions of bridge structures contained in coal, this hypothesis being supported partially by the fact that lower rank coals have rich amount of easily cleavable bonds such as ether bonds due to their higher contents of oxygen.

It is interesting to note that in the reaction at 420 °C, the amounts of hydrogen transferred from DHP were larger than those from DHA, while at 380 °C, DHA tended to donate more amounts of hydrogen to coal than DHP did. It is reasonable, at first, that at 420 °C amounts of hydrogen transferred are larger than that at 380 °C because cleavage reactions took place extensively at higher temperature. As for interesting behavior of DHP and DHA, we can say that the bond cleavage reaction occurred during the heat-treatment is dependent on the type of the hydrogen donating compounds. Therefore, in order to compare the reactivity of the hydrogen donating compounds, DHA and DHP, we conducted the reaction of the coal model compounds which have the bridges between the aromatic moieties, such as 1,2-diphenylethane and so on with the hydrogen donating compounds under the similar conditions to the reaction with coal

Homolytic cleavage reaction of dimethylene and methylene-ether bonds.

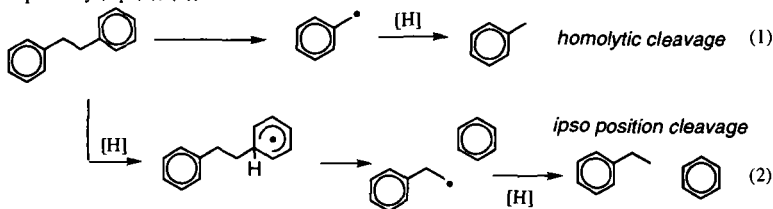
Generally, coal macromolecule is considered to consist of aromatic cluster and alkyl bridges or side chains including naphthenic portion, being regarded as cross-linking polymers as a whole. In the proposed coal chemical structure models, there observed the bridge structures between two aromatic rings, such as $-\text{CH}_2-\text{CH}_2-$, $-\text{CH}_2-\text{O}-$ or $-\text{CH}_2-$ and so on, these seeming to be important in the thermochemical reaction. On the basis of this background, we employed 1,2-diphenylethane (DPE), benzylphenylether (BPE), and 1,2-di(1-naphthyl)ethane (DNE) as coal model compounds having the bridge structures.

The heat-treatment of these compounds in the presence of DHA or DHP was conducted under the similar conditions to that of coal. It was found that the conversion of BPE was rather high (> 95 %) while those of DPE and DNE were low (< 6 %). The bridge structure in coal is thought to be cleaved more easily than those in DPE or DNE were because of the relatively large size and many substituents of coal aromatic rings which can assist, in general, the cleavage reactions. On the other hand, rather high reactivity of BPE with homolytic fission of bridge bond can be easily understood because bond dissociation energy of carbon-oxygen is low. Here, in order to observe much more difference of the reactivities of DPE and DNE in either DHA or DHP, the reaction time was prolonged as 60 min. The reaction temperature of BPE was set to 380 °C for 5 min because BPE was found to be more reactive than DPE or DNE.

Figure 2 shows the results of the reactions in the presence of two different hydrogen donors. Under these conditions, considerable amounts of DHA or DHP were converted in each blank run so that the yield of anthracene or phenanthrene would not properly reflect the exact amount of DHA or DHP consumed for hydrogen transfer. Therefore, we evaluate the degree of the bond cleavage reaction on the basis of the yields of the cleaved products. The conversion of the model compounds reflects the strength of cleavable bonds (order of bond dissociation energy is $\text{PhCH}_2-\text{OPh} \ll \text{NapCH}_2-\text{CH}_2\text{Nap} < \text{PhCH}_2-\text{CH}_2\text{Ph}$). DPE showed less reactivity even under these conditions (420 °C, 60 min), and slightly higher yield of toluene when DHP was used as the hydrogen donor than in the case of DHA. Actually, the same trend was observed with the reaction of DNE at 420 °C for 5 min. It is thought that the less reactivity of DPE might be caused by the small size of aromatic rings and the absence of substituents like $-\text{OH}$ or alkyl groups, however, much more reactivity would be expected with bridge bonds contained in the structure of coal. On the other hand, it should be noted that yields of the homolytic cleavage products from DNE or BPE, 1-methylnaphthalene or toluene and phenol, respectively, were higher when DHA was used than in the case of DHP. These results remind us that DHA has the higher potential to scavenge the radical generated.

Ipsso position cleavage reaction of the bridge structure in model compounds.

In the reactions of DPE and DNE, there also observed the formation of the ipsso position cleavage products like benzene and ethylbenzene, and naphthalene and ethylnaphthalene, respectively (eq. (1), (2)).



The reaction of DPE or DNE with two different hydrogen donors at 420 °C for 60 min gave the ipsso position cleavage products in 0.1-6.6% yield (Figure 3). These yields from the reaction using DHP were considerably higher than the case of DHA. In the case of BPE, only homolytic

cleavage reaction occurred. However, the yields of the ipso position cleavage products were relatively low in comparison with those of the homolytic cleavage products. Here we would like to refer to the reports concerning bridge bonds contained in coal[11]. RuO₄ oxidation reaction confirmed that, in coal, dimethylene bridge connecting two aromatic moieties exists because the formation of succinic acid was observed in the oxidized products of COM. The presence of succinic acid shows the presence of dimethylene bridge. However, as for monomethylene bridge this oxidation could not confirm its presence in COM because under these oxidation conditions, the malonic acid is unstable. In generally speaking, the prevailing presence of monomethylene bridge bond in COM is supported by many coal researchers. Then, we employed 1,5-dibenzyl-naphthalene (DBN) as the possible substrate of coal model compounds. It does not have homolytic cleavable linkages like -CH₂-CH₂- or -CH₂-O-, so only the ipso position cleavage is expected to take place. Its reaction afforded benzene, toluene, benzylnaphthalene and benzyl-methylnaphthalene. However, only small amount of naphthalene derivatives was obtained and the recovery of the substrate was not so high. This could be explained by assuming that some oligomerization or very complicated reaction might occur under the reaction conditions as we had pointed out in a previous paper[3]. Therefore, we judged the degree of cleavage on the basis of the sum of the yield of benzene and toluene. Also from this result, the ipso position cleavage by using DHP could proceed more efficiently than in the case of DHA. In this system, strong C_{alkyl}-C_{aryl} bond must be cleaved by solvent induced scission. It could be suggested that introduction of hydrogen atom as a result of radical hydrogen transfer or free hydrogen transfer occurred in heat-treatment of coal, and Malhotra et al. also mentioned the effectiveness of ipso position cleavage in liquefaction reaction[12].

Consideration about the bond cleavage reaction of the bridge structures in coal.

In the reactions of coal with DHA or DHP, at 420 °C, DHP had been consumed at larger amounts and at 380 °C, DHA was the case as shown in Figure 1. As we had already mentioned, we thought that these consumption of hydrogen donor could correlate to the degree of bond cleavage reaction occurred in coal. Although we know that the reactions during heat-treatment would be so complex that they could not be described simply, the bond cleavage reactions of the bridge structures in coal proceeded mainly under our conditions.

If we here assume that with higher rank coal in the present study, monomethylene bridge prevails, we can easily understand the results shown in this paper. At 420 °C for 5 min, DHP shows higher extent of hydrogen transfer than that of DHA, and DHP is favorable to DHA as for ipso position cleavage and above observation is readily understood by referring to the assumption that methylene bridge is prevailing bridge bond than more longer methylene bridges. At 380 °C, carbon-oxygen related bond is cleaved so that DHA is effective hydrogen transfer reagent than DHP. Therefore, we can say that there is a possibility to use DHP or DHA as the probe to understand the reactivity and structure of coal.

ACKNOWLEDGMENT

This work was partially supported by a Grant-in-aid provided by the Iron and Steel Institute of Japan, and the authors acknowledge the support of Sumitomo Metal Industries Ltd. for useful discussion.

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Table 1. Ultimate and proximate analyses of the sample coals

Coal	Proximate analyses (wt%, db)			Ultimate analyses (wt%, daf)				
	Ash	VM	FC	C	H	N	S	O ^a
Lusca	9.5	23.5	67.0	88.3	4.6	1.5	0.3	5.3
Goonyella	9.8	23.4	66.8	88.1	5.1	1.9	0.6	4.3
Pittstone-M	7.3	34.3	58.4	85.7	5.5	1.7	1.0	6.1
Workworth	13.8	34.2	52.0	84.7	5.9	1.8	0.6	7.0
Witbank	8.0	32.9	59.1	82.7	4.5	2.2	0.6	10.0
K-Prima	3.8	43.4	52.8	81.2	5.9	1.3	0.4	11.2

^a By difference

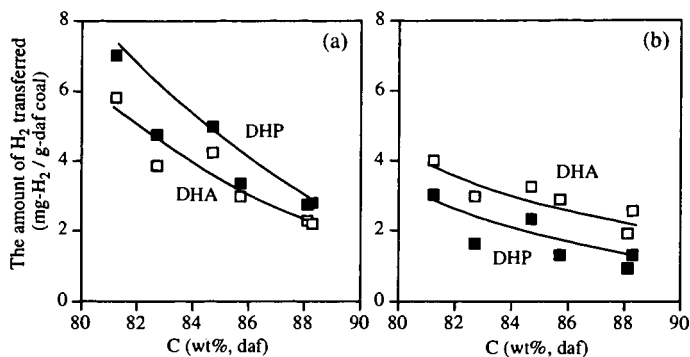


Figure 1. Evaluated amount of hydrogen transferred from DHA (□) or DHP (■) to coal at (a) 420 °C and (b) 380 °C

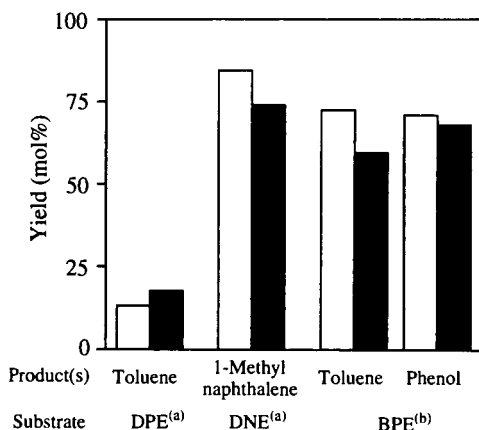


Figure 2. The yields of the homolytic cleavage products in the reaction of Ar-CH₂-X-Ar (X=CH₂, O) in the presence of hydrogen donor, DHA (□) or DHP (■): (a) 420 °C, 60 min, [Substrate]:[donor]=0.25:0.25 (in mmol), (b) 380 °C, 5 min, [Substrate]:[donor]=0.25:0.25 (in mmol)

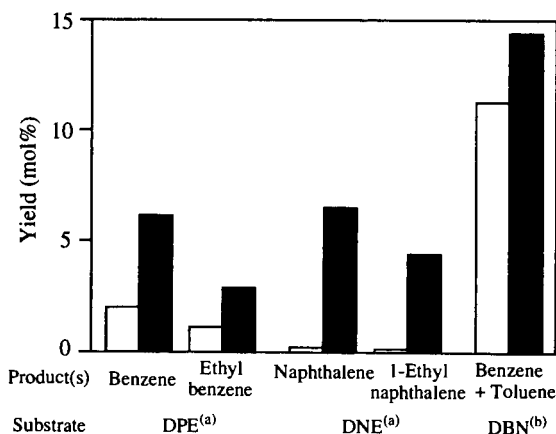


Figure 3. The yields of the ipso position cleavage products in the reaction of DPE, DNE and DBN in the presence of DHA (□) or DHP (■): (a) 420 °C, 60 min, [Substrate]:[donor]=0.25:0.25 (in mmol), (b) 430 °C, 60 min, [Substrate]:[donor]=0.25:0.25 (in mmol)